

DECLARATION

I, Taijiro Ogawa of c/o SHIGA INTERNATIONAL PATENT OFFICE, 2-3-1 Yaesu, Chuo-ku, Tokyo 104-8453 JAPAN, understand both English and Japanese, am the translator of the English document attached, and do hereby declare and state that the attached English document contains an accurate translation of the official certified copy of Japanese Patent Application No(s).2002-152699 and that all statements made herein are true to the best of my knowledge.

Declared in Tokyo, Japan

This *1st day of December, 2004*

Taijiro Ogawa

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JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Applicant(s) : Tokyo Ohka Kogyo Co., Ltd.

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[Document Type] Specification

[Title of the Invention] Negative Resist Composition

[Claims]

[Claim 1] An alkali-developable negative resist composition comprising a compound (A) which generates an acid upon exposure to radiation, and a resin component (B) which is made insoluble in alkali under the action of an acid, wherein the component (B) is a resin component containing:

(b1) a unit which becomes insoluble in an alkali solution as a result of the formation of a lactone under the action of an acid generated from the component (A), and

(b2) a unit having an alcoholic hydroxyl group.

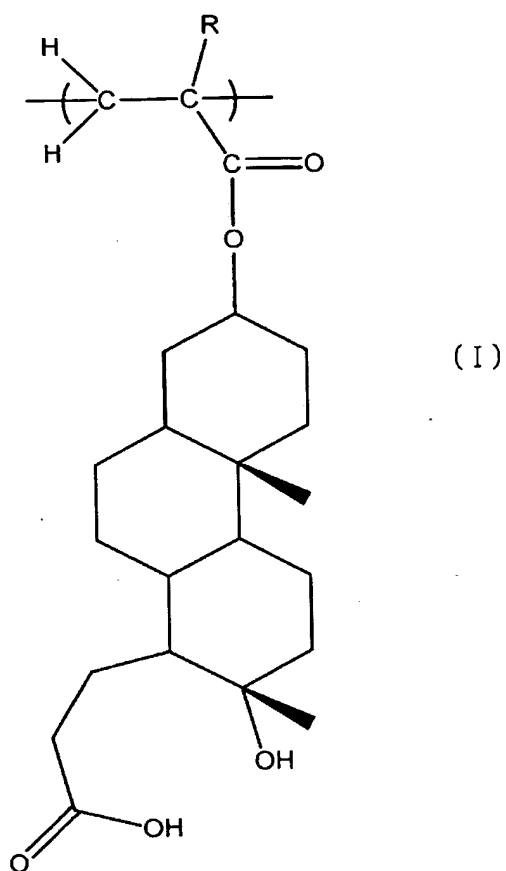
[Claim 2] The negative resist composition according to claim 1, wherein the lactone is δ -lactone.

[Claim 3] The negative resist composition according to claim 2, wherein the unit (b1) is a unit derived from a (meth)acrylate ester having δ -hydroxy acid bonded to a non-aromatic polycyclic hydrocarbon group.

[Claim 4] The negative resist composition according to claim 3, wherein the non-aromatic polycyclic hydrocarbon group is a group in which two hydrogen atoms are eliminated from a non-substituted or methyl-substituted tricycloalkane.

[Claim 5] The negative resist composition according to claim 4, wherein the unit (b1) is a unit represented by the following general formula (I):

[Chemical Formula 1]

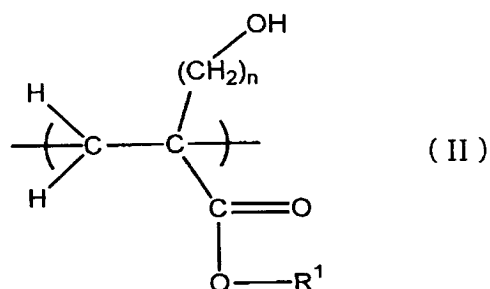


(wherein R represents a hydrogen atom or a lower alkyl group) .

[Claim 6] The negative resist composition of one of claims 1 to 5, wherein the unit (b2) is (i) a unit derived from an α -hydroxyalkyl (methyl)acrylate ester.

[Claim 7] The negative resist composition according to claim 6, wherein the unit (b2) is a unit represented by the following general formula (II):

[Chemical Formula 2]



(wherein R^1 represents a lower alkyl group, a non-aromatic polycyclic alkyl group, a hydroxyl group-containing non-aromatic polycyclic alkyl group or a lactone-containing non-aromatic polycyclic alkyl group, and n represents an integer of 5 or less).

[Claim 8] The negative resist composition according to claim 7, wherein R^1 is a lower alkyl group.

[Claim 9] The negative resist composition according to claim 8, wherein R^1 is a methyl group.

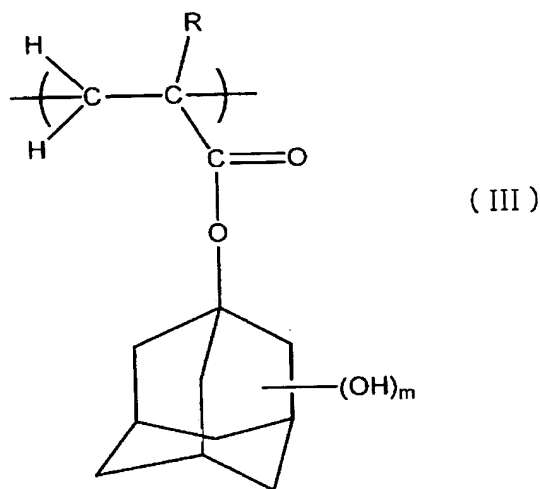
[Claim 10] The negative resist composition according to one of claims 7 to 9, wherein n is 1.

[Claim 11] The negative resist composition according to one of claims 1 to 5, wherein the unit (b2) is a unit derived from a hydroxyl group-containing non-aromatic polycyclic alkyl ester of (meth)acrylic acid.

[Claim 12] The negative resist composition according to claim 11, wherein the hydroxyl group-containing non-aromatic polycyclic alkyl ester group, which constitutes the hydroxyl group-containing non-aromatic polycyclic alkyl ester, is an adamantyl group having at least one hydroxyl group.

[Claim 13] The negative resist composition according to claim 12, wherein the unit (b2) is a unit represented by the following general formula (III):

[Chemical Formula 3]



(wherein R represents a hydrogen atom or a lower alkyl group, and m represents an integer of 1 to 3).

[Claim 14] The negative resist composition according to claim 13, wherein one hydroxyl group exists and the hydroxyl group is bonded to the adamantanyl group at the 3-position in the general formula (III).

[Claim 15] The negative resist composition according to any one of claims 1 to 14, wherein the component (B) is a copolymer containing the unit (b1) and the unit (b2) in a molar ratio of 1:9 to 9:1.

[Claim 16] The negative resist composition according to one of claims 1 to 15 dissolved in a solvent (C), the solvent C including water.

[Claim 17] The negative resist composition according to claim 16, wherein the solvent (C) contains propylene glycol monomethyl ether and water.

[0001]

[Technical Field of the Invention]

The present invention relates to a negative resist composition.

[0002]

[Prior Art]

Various proposals have hitherto been made for chemical amplification type negative resist compositions. For a resist for exposure light having a wavelength equal to or shorter than that of an ArF excimer laser, a technique of forming a negative pattern by being made insoluble in an alkali solution as a result of intermolecular or intramolecular formation of lactone in a base resin (Japanese Patent Application, First Publication No. 2000-206694) is effective. Similarly, Japanese Patent Application, First Publication No. 2001-174993 discloses a negative resist composition comprising a specific resin component having excellent lactone-forming ability. Such a negative resist composition has a chemical structure which contributes to sufficient transparency to light in the far ultraviolet region including ArF excimer laser light having a wavelength of 193 nm and high dry etching resistance.

[0003]

[Problems to be Solved by the Invention]

In addition, an alkali concentration of a standard alkali developing solution used in the manufacture of electronic parts such as semiconductor devices and liquid crystal devices is 2.38% by mass. Typical alkali developing solutions include, for example, aqueous solutions and the like of tetramethylammonium hydroxide (abbreviation: TMAH). Although the alkali developing solution having such an alkali concentration can be used in manufacturing lines for electronic parts after being diluted to some extent, the dilution limit is considered to be about 0.1% by mass or higher.

On the other hand, the negative resist composition disclosed in the latter has a problem in that it is likely to swell in an alkali developing solution, and a resist pattern having a good profile can be formed by using an alkali developing solution having a low alkali concentration such as 0.05% by mass or less. That is, when developing with an

alkali developing solution having a practical alkali concentration of 0.1% by mass or more, a resin component, which becomes insoluble in an alkali solution upon exposure to light, swells, and thus a resist pattern having a good profile cannot be formed.

[0004]

Under these circumstances, the present invention has been made, and an object thereof is to provide a negative resist composition which is less likely to swell in an alkali developing solution.

[0005]

[Means for Solving the Problem]

To achieve the above object, the negative resist composition of the present invention is an alkali-developable negative resist composition comprising a compound (A) which generates an acid upon exposure to radiation, and a resin component (B) which becomes insoluble in alkali solution under the action of an acid, wherein the component (B) is a resin component containing:

- (b1) a unit which becomes insoluble in an alkali solution as a result of the formation of lactone under the action of an acid generated from the component (A), and
- (b2) a unit having an alcoholic hydroxyl group.

[0006]

[Embodiments of the Invention]

The respective constitutions of the negative resist composition of the present invention will now be described in detail.

<Compound (A) which generates an acid upon exposure to radiation>

The component (A) is a so-called acid generator.

The component (A) can be appropriately selected from known acid generators used in a conventional chemical amplification type negative resist.

Among these acid generators, an onium salt containing a halogen-substituted alkylsulfonic acid ion as an anion is particularly preferable.

The cation of the onium salt is preferably mono- or diphenyl iodonium, or mono-, di-, or triphenyl phosphonium, which may be substituted or may not be substituted with a

lower alkyl group such as methyl group, ethyl group, propyl group, n-butyl group or tert-butyl group, or a lower alkoxy group such as methoxy group or ethoxy group; or dimethyl (4-hydroxynaphthyl) sulfonium.

In addition, the anion of the onium salt is preferably a fluoroalkylsulfonic acid ion wherein a portion or all of hydrogen atoms of an alkyl group having about 1 to 15 carbon atoms are substituted with a fluorine atom.

In particular, a fluoroalkylsulfonic acid ion wherein all of the hydrogen atoms of an alkyl group having 1 to 10 carbon atoms are substituted with a fluorine atom is preferable. The reason is that the strength of sulfonic acid decreases as the carbon chain becomes longer and the fluorination ratio (proportion of fluorine atoms in the alkyl group) decreases.

[0007]

Specific examples of the onium salt include trifluoromethane sulfonate or nonafluorobutane sulfonate of diphenyl iodonium, trifluoromethane sulfonate or nonafluorobutane sulfonate of bis(4-tert-butylphenyl)iodonium, trifluoromethane sulfonate or nonafluorobutane sulfonate of triphenyl sulfonium, trifluoromethane sulfonate or nonafluorobutane sulfonate of tri(4-methylphenyl)sulfonium, trifluoromethane sulfonate or nonafluorobutane sulfonate of dimethyl(4-hydroxynaphthyl)sulfonium, trifluoromethane sulfonate or nonafluorobutane sulfonate of monophenyldimethyl sulfonium and trifluoromethane sulfonate or nonafluorobutane sulfonate of diphenylmonomethyl sulfonium.

As the component (A), these acid generators can be used alone, or two or more kinds thereof can be used in combination.

[0008]

The component (A) is used in an amount within a range from 0.1 to 30 parts by mass, preferably from 0.5 to 20 parts by mass, and more preferably from 1 to 10 parts by mass, based on 100 parts by mass of the component (B). When the amount is less than the lower limit, no image is likely to be formed. On the other hand, when the amount exceeds 30 parts by mass, it is not easy to obtain a uniform solution and the storage

stability is likely to be impaired.

[0009]

<Resin component (B) which becomes insoluble in an alkali solution under the action of an acid>

The component (B) is a resin component containing:

(b1) a unit which becomes insoluble in an alkali solution as a result of the formation of lactone under the action of an acid generated from the component (A), and
(b2) a unit having an alcoholic hydroxyl group.

The component (B) is not specifically limited as long as it contains the unit (b1) and the unit (b2) and may be, for example, a copolymer (which may be either a block copolymer or a random copolymer) containing the unit (b1) and the unit (b2), or a mixture of a polymer which contains the unit (b1) but does not contain the unit (b2) and a polymer which contains the unit (b2) but does not contain the unit (b1). The former copolymer is preferable and a random copolymer is more preferable.

The molar ratio of the unit (b1) to the unit (b2) is preferably within a range from 1:9 to 9:1, and more preferably from 4:6 to 3:7, because a resist pattern, which is superior in definition and causes less swelling, is formed as the amount of the latter increases.

[0010]

The component (B) may contain other units, in addition to the unit (b1) and the unit (b2), but to obtain the effect of the present invention, the total amount of the unit (b1) and the unit (b2) is 50 mol% or more, and preferably 70 mol% or more, based on the component (B).

An aspect containing other units includes, for example, the case wherein the other units are contained in a copolymer (which may be either a block copolymer or a random copolymer) of one or both of the unit (b1) and the unit (b2), or the case wherein a homopolymer containing the other unit is mixed with a resin component containing the unit (b1) and the unit (b2). In particular, a terpolymer or tetrapolymer composed of the unit (b1), the unit (b2) and one or two kinds of the other units is preferable, and a random copolymer is more preferable.

[0011]

In addition, the mass-average molecular weight of the component (B) is within a range from about 1500 to 10000, and preferably from about 2000 to 5000.

[0012]

-Unit (b1)

The unit (b1) is a unit which becomes insoluble in an alkali solution as a result of the formation of lactone under the action of an acid generated from the component (A).

To form such a lactone, it is necessary to have two kinds of functional groups capable of reacting with each other to form lactone in the molecule. In addition, when these functional groups are dehydrated under the action of an acid generated from the component (A) to form a lactone, the unit (b1) becomes insoluble in an alkali solution, and thus the entire component (B) becomes insoluble in an alkali solution.

Two kinds of functional groups capable of reacting with each other to form a lactone include, for example, a combination of a hydroxyl group and a carboxyl group. For example, those having a hydroxyl group and a carboxyl group on the side chain of a main resin skeleton (hereinafter sometimes referred to as a lactone precursor unit) are preferable.

[0013]

Since the main resin skeleton can be easily synthesized at a low price, it is preferably a unit derived from (meth)acrylic acid. The unit (b1) is preferably a unit wherein hydrogen atoms of the carboxyl group of the unit derived from (meth)acrylic acid are substituted with a group having the two functional groups.

In the present specification, (meth)acrylic acid includes acrylic acid and/or methacrylic acid.

As lactone formed as a result of dehydration under the action of an acid generated by the acid generator as described above, any of β -lactone, γ -lactone and δ -lactone can be used. That is, the unit (b1) preferably has any of β -hydroxy acid, γ -hydroxy acid and δ -hydroxy acid.

However, because of the high stability and the high lactone-forming ability of

hydroxy acid before reacting with the component (A), a group having δ -lactone, i.e., δ -hydroxy acid is preferable.

[0014]

The unit (b1) is more preferably a unit derived from a (meth)acrylate ester having δ -hydroxy acid bonded to a non-aromatic polycyclic hydrocarbon group. The use of such a unit (b1) exerts the effect of enhancing the transparency to exposure light and the definition and increasing the carbon density in the component (B) thereby to improve the dry etching resistance. As described above, when the non-aromatic polycyclic hydrocarbon group is bonded to the main resin skeleton, a distance between the main resin skeleton and two functional groups increases, thus making it possible to prevent the occurrence of the undesired side reaction.

The non-aromatic polycyclic hydrocarbon group is not specifically limited, and there can be used those which are commonly used in resists for ArF excimer lasers, and examples thereof include crosslinking polycyclic cyclic hydrocarbon groups such as bicyclo[2.2.1]heptyl group, bornyl group, adamantyl group, tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodecyl group and tricyclo[5.2.1.0^{2,6}]decyl group.

[0015]

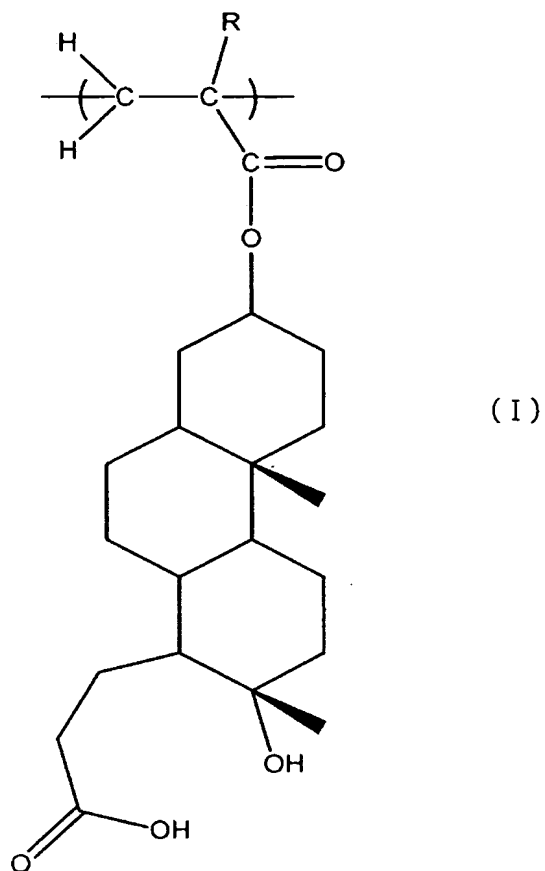
In particular, the unit (b1) wherein the non-aromatic polycyclic hydrocarbon group is a group obtained by eliminating two hydrogen atoms from non-substituted or methyl-substituted tricycloalkane is preferable because it can be inexpensively and easily synthesized.

[0016]

More specifically, the unit (b1) is more preferably a unit represented by the following general formula (I):

[0017]

[Chemical Formula 4]



[0018]

(R represents a hydrogen atom or a lower alkyl group).

The lower alkyl group includes, for example, a straight-chain or branched alkyl group having 1 to 5 carbon atoms, and preferably 1 to 3 carbon atoms. Specific examples thereof include methyl group, ethyl group, propyl group, isopropyl group, n-butyl group, sec-butyl group, tert-butyl group and amyl group.

[0019]

-Unit (b2)

The unit (b2) is a unit having an alcoholic hydroxyl group and is preferably a unit having, for example, the alcoholic hydroxyl group in the main resin skeleton or on the side chain.

So that the main resin skeleton can be easily synthesized, it is preferably a unit

derived from (meth)acrylic acid, for example.

In addition, the alcoholic hydroxyl group may be (i) an alcoholic hydroxyl group which is directly bonded to the resin skeleton in the form of a hydroxyalkyl group, or (ii) an alcoholic hydroxyl group which is bonded through an ester in the form of a hydroxyl group-containing non-aromatic polycyclic alkyl group. In the case of the former (i), it is preferably bonded to the acrylate ester at the α -position.

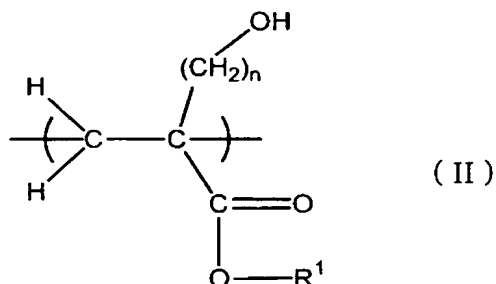
[0020]

In particular, the unit (b2) containing the former (i) is a unit derived from an α -hydroxyalkyl(meth)acrylate ester.

In particular, it is more preferable to use the unit (b2) represented by the following general formula (II):

[0021]

[Chemical Formula 5]



[0022]

(In this formula, R^1 represents a lower alkyl group, a non-aromatic polycyclic alkyl group, a hydroxyl group-containing non-aromatic polycyclic alkyl group or a lactone-containing non-aromatic polycyclic alkyl group, and n represents an integer of 5 or less.)

[0023]

In R^1 , the lower alkyl group may be a straight-chain or branched alkyl group having 5 or fewer carbon atoms. Examples thereof include methyl groups, ethyl groups, propyl groups, isopropyl groups, *n*-butyl groups, *sec*-butyl groups, *n*-butyl groups, amyl groups, and the like, and a methyl group is preferable.

Non-aromatic polycyclic alkyl groups which are used in the resists for ArF excimer lasers can be used, and examples thereof include crosslinking polycyclic cyclic alkyl groups such as bicyclo[2.2.1]heptyl group, bornyl group, adamantyl group, tetracyclo[4.4.0.1^{2.5}.1^{7.10}]dodecyl group and tricyclo[5.2.1.0^{2.6}]decyl group.

In addition, the hydroxyl group-containing non-aromatic polycyclic alkyl group includes, for example, those wherein at least one hydroxyl group is bonded to the crosslinking polycyclic cyclic alkyl group, and specific examples thereof include adamantanol.

In addition, the lactone-containing non-aromatic polycyclic alkyl group includes, for example, those wherein lactone is bonded to the groups exemplified in the non-aromatic polycyclic alkyl group.

The unit (b2) having a non-aromatic polycyclic alkyl group, a hydroxy-containing non-aromatic polycyclic alkyl group or a lactone-containing non-aromatic polycyclic alkyl group is effective to enhance dry etching resistance and adhesion between the substrate and the resist layer.

[0024]

In formula (II), the n in $-(CH_2)_n-$ is an integer of 1 to 5. Examples thereof include methylene groups, ethylene groups, propylene groups and n -butylene groups, and methylene groups are preferable.

[0025]

The unit (b2) containing (ii) is a unit derived from a hydroxyl group-containing non-aromatic polycyclic alkyl ester of (meth)acrylic acid, and is preferable in view of improvement in dry etching resistance.

The hydroxyl group-containing non-aromatic polycyclic alkyl group to be bonded to the ester includes, for example, those used in resists for ArF excimer lasers, in which a hydroxyl group is bonded to a non-aromatic polycyclic alkyl group. Specific examples thereof include those wherein a hydroxyl group is bonded to crosslinking polycyclic cyclic alkyl groups such as bicyclo[2.2.1]heptyl groups, bornyl groups, adamantyl groups, tetracyclo[4.4.0.1^{2.5}.1^{7.10}]dodecyl groups and tricyclo[5.2.1.0^{2.6}]decyl groups. One or

more hydroxyl groups are bonded and, preferably, 1 to 3 hydroxyl groups are bonded.

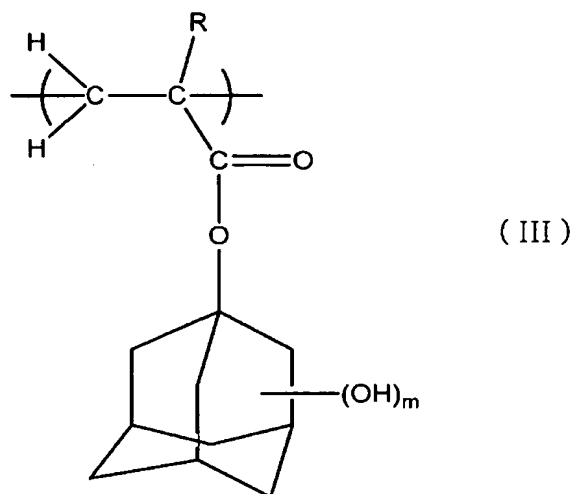
[0026]

Particularly, the hydroxyl group-containing non-aromatic polycyclic alkyl group is preferably an adamantyl group having at least one hydroxyl group.

Furthermore, the unit (b2) is preferably a unit represented by the following general formula (III):

[0027]

[Chemical Formula 6]



[0028]

(In this formula, R has the same meaning as in the formula (I), and m represents an integer of 1 to 3.)

[0029]

Although m represents an integer of 1 to 3, it is more preferably 1. In addition, the hydroxyl group is preferably bonded to the adamantyl group at the 3-position. Therefore, it is preferable to have one hydroxyl group that is also bonded to the adamantyl group at the 3-position.

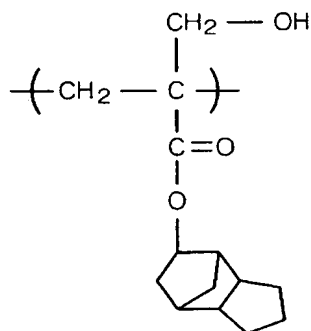
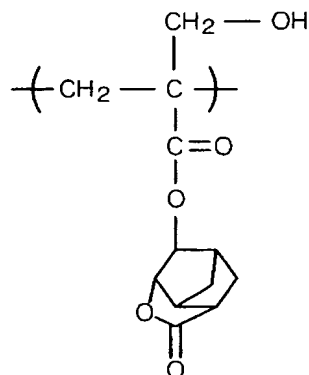
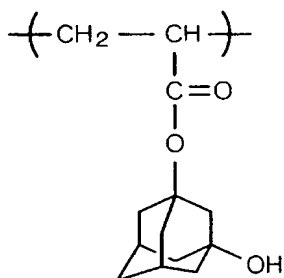
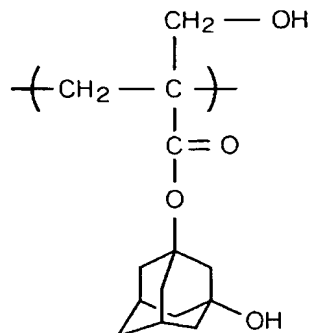
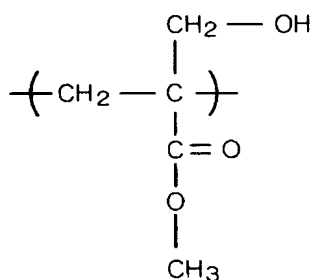
[0030]

The units and the like shown in [Chemical Formula 7] can be given as preferable

embodiments of unit (b2).

[0031]

[Chemical Formula 7]



[0032]

-Other units

Other units which are optionally contained in the component (B), in addition to the unit (b1) and the unit (b2), are not specifically limited as long as the effects of the present invention are not impaired. Other units include, for example, those having a resin skeleton of (meth)acrylic acid.

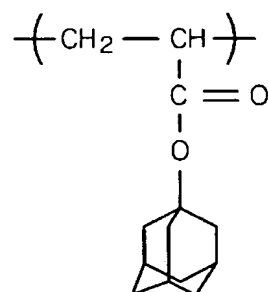
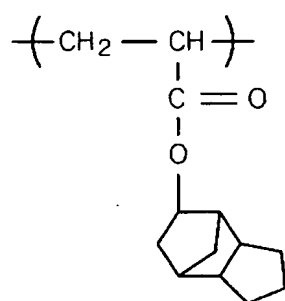
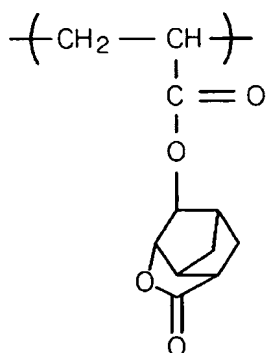
Specific examples thereof include those wherein a non-aromatic polycyclic hydrocarbon group or a non-aromatic polycyclic hydrocarbon group containing lactone is ester-bonded to the resin skeleton.

The non-aromatic polycyclic hydrocarbon group and the non-aromatic polycyclic hydrocarbon group containing lactone are not specifically limited and there can be used the same groups as exemplified in the description of the unit (b2).

Specific examples thereof include units shown in the following [Chemical Formula 8].

[0033]

[Chemical Formula 8]



[0034]

The component (B) can be prepared by a conventional well-known method.

A copolymer of the unit (b1) and the unit (b2) can be obtained, for example, by radical polymerizing a monomer (b1)' corresponding to a precursor of the unit (b1) with a monomer (b2)' corresponding to a precursor of the unit (b2).

The monomer (b2)' is sold on the market and is easily commercially available.

The monomer (b1)' can be obtained, for example, with reference to a known method. For example, androsterone is esterified with (meth)acrylic acid chloride in the

presence of a basic catalyst to obtain an esterified compound. Then, the esterified compound is oxidized by a known method using hydrogen peroxide or the like to form lactone and the resulting lactone is hydrolyzed with alkali, thereby causing a ring opening to obtain a monomer (b1)'.

[0035]

<Solvent (C)>

The negative resist composition of the present invention is preferably used in a form wherein the component (A), the component (B), and the optionally mixed other components described hereinafter, are dissolved in the solvent (C).

Examples of the solvent (C) include known organic solvents, for example, ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl isoamyl ketone and 2-heptane; polyhydric alcohols and derivatives thereof, such as ethylene glycol, ethylene glycol monoacetate, diethylene glycol, diethylene glycol monoacetate, propylene glycol, propylene glycol monoacetate, dipropylene glycol or dipropylene glycol monoacetate, or monomethyl ether, monoethyl ether, monopropyl ether, monobutyl ether or monophenyl ether thereof or derivatives thereof, and of these preferably propylene glycol monomethyl ether (abbreviation: PGME) and propylene glycol monomethyl ether acetate (abbreviation: PGMEA); cyclic ethers such as dioxane; esters such as methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate and ethyl ethoxypropionate; and amide type solvents such as N,N-dimethylformamide, N,N-dimethylacetamide and N-methyl-2-pyrrolidone.

These solvents may be used alone, or two or more kinds thereof may be used in combination.

[0036]

It is preferable to mix water with the solvent (C) because the stability over time of the resist composition is improved. In view of the effect, the amount of water is controlled within a range from 5 to 20% by mass, and preferably from 5 to 15% by mass, based on 100% by mass of the organic solvent contained in the solvent (C) (for example, organic solvent selected from one, two or more kinds of the organic solvents described

above).

In particular, a mixed solvent of PGME and water is preferable and water is mixed with PGME in an amount within a range from 5 to 20% by mass, and preferably from 5 to 15% by mass, because the resulting negative resist composition is superior in stability over time.

[0037]

The component (B) generally has good solubility in a commonly used solvent (particularly PGMEA or PGME) for the resist and also has the effect of improving the storage stability of the negative resist composition.

[0038]

<Other components>

To the negative resist composition of the present invention, commonly used miscible additives such as additional resins, plasticizers, stabilizers, colorants, surfactants and amines can be optionally added to improve performances of the resist film.

[0039]

<Method for use of negative resist composition>

The negative resist composition of the present invention can be applied, for example, to a resist pattern forming method of a conventional photoresist technique.

In order to suitably carry this out, a solution of the negative resist composition of the present invention is applied on a substrate such as silicon wafer using a spinner, and this is then dried to form a photosensitive layer. The substrate is not specifically limited and may be various substrates on which a conventional negative resist is applied, for example, a silicon wafer, a silicon wafer on which an organic or inorganic type antireflection film is provided, and a glass substrate.

Furthermore, the substrate having a photosensitive layer formed thereon is exposed to KrF excimer laser light, ArF excimer laser light, F₂ excimer laser light, EUV (Extreme ultraviolet light), electron rays, soft X-rays, or X-rays through a desired mask pattern using a reducing-type projection aligner, or is directly formed with a pattern, and is then heated.

The exposed substrate is developed with a developing solution such as an aqueous alkali solution. An image faithful to the mask pattern can be obtained by this forming method.

[0040]

The developing solution is not specifically limited and a commonly used aqueous alkali solution can be used.

The negative resist composition of the present invention has an effect such that it is less likely to swell in an alkali developing solution as compared with a conventional one, and thus a resist pattern having a good profile can be obtained. For example, when using an aqueous solution of TMAH, the alkali concentration of the developing solution is controlled within a range from 0.05 to 2.38% by mass, and preferably from 0.1 to 0.5% by mass.

[0041]

[Examples]

The present invention will be described in detail by way of examples.

<Examples 1 to 4 (TMAH concentration: 0.05% by mass)>

Component (A):

Triphenylsulfonium trifluoromethane sulfonate	1 part by mass
Triphenylsulfonium nonafluorobutane sulfonate	0.68 parts by mass

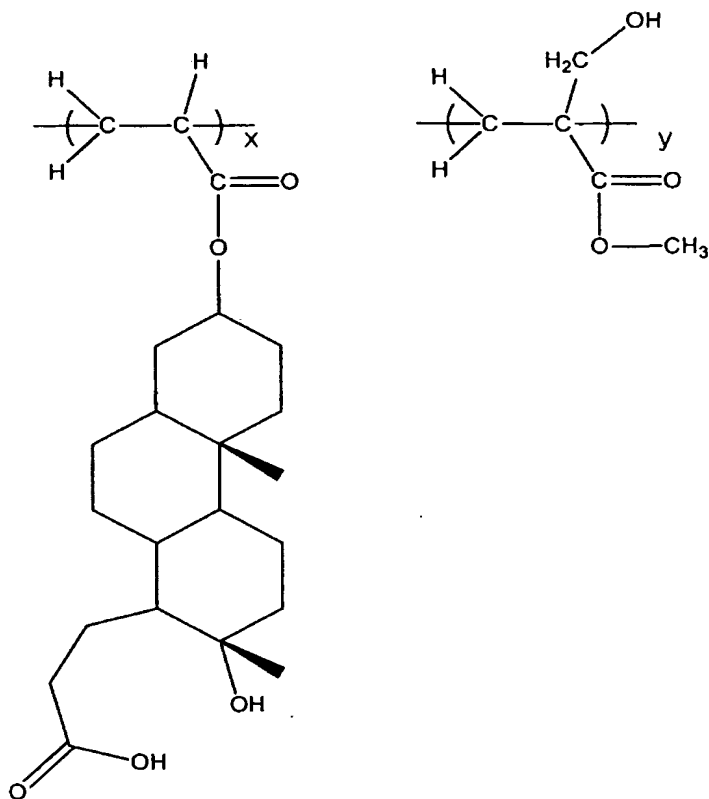
Other components:

4-phenylpyridine	0.2 parts by mass
Fluorine-silicon type surfactant R08 (manufactured by DAINIPPON INK & CHEMICALS Co., Ltd.)	0.1 parts by mass

The component (A) and other components described above as well as 100 parts by mass of the component (B) (resin component: random copolymer) represented by the following structural formula:

[0042]

[Chemical Formula 9]



[0043]

described in Table 1 were dissolved in a mixed solvent of 1200 parts by mass propylene glycol monomethyl ether and 100 parts by mass of water to obtain a uniform negative resist solution (negative resist composition).

[0044]

On a silicon wafer, an organic antireflection film AR-19 (manufactured by Shipley Co.) was formed in a thickness of 82 nm by heating at 215°C for 60 seconds, and then the above resist solution was applied on the antireflection film using a spinner and was dried on a hot plate at 100°C (prebaking) for 60 seconds to form a resist layer having a thickness of 300 nm.

Using an ArF exposure apparatus NSR-S302 (manufactured by Nikon Corporation, NA = 0.60), the silicon wafer having a resist layer formed thereon was

selectively exposed to an ArF excimer laser (193 nm) through a mask, and was then subjected to a post-exposure baking (PEB) treatment at 100°C for 60 seconds.

The exposed silicon wafer was developed with an aqueous tetramethylammonium hydroxide solution having a concentration of 0.05% by mass at 23°C for 30 seconds, washed with water, dried, and then post-baked at 100°C for 60 seconds.

[0045]

Resolution limit of the resist pattern obtained by the operation, cross sectional profile (represented by line width (nm) and its orthogonality of resist; the same shall apply hereinafter) of the resist pattern, and resist pattern size, sensitivity and degree of swelling at the profile are summarized in Table 1. In the table, the symbol “L&S” means a line-and-space pattern.

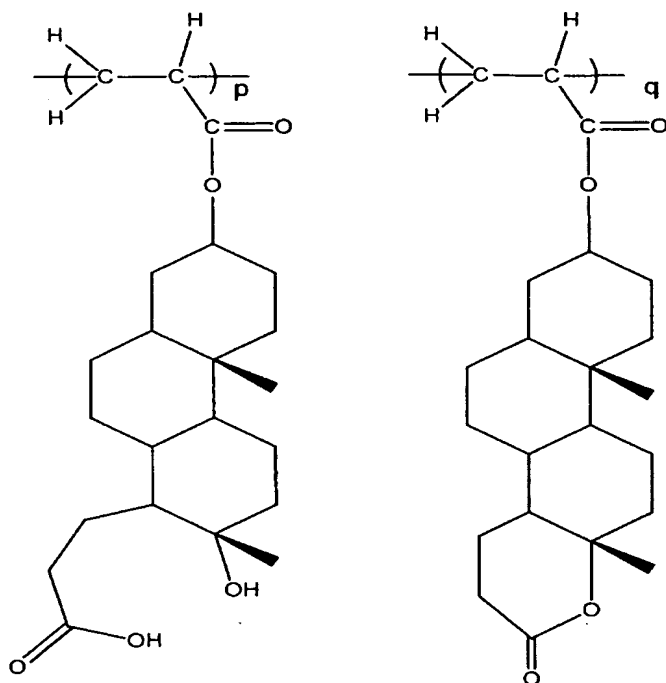
[0046]

<Comparative Example 1 (TMAH concentration: 0.05% by mass)>

In the same manner as in Example 1, except that the resin component was replaced by a polymer (random copolymer represented by the following structural formula:

[0047]

[Chemical Formula 10]



[0048]

described in Table 1 Example 1, a negative resist solution was obtained.

The same operation as in Example 1 was conducted to form a resist pattern. Resolution limit of the resist pattern obtained by the operation, cross sectional profile of the resist pattern, and resist pattern size, sensitivity and degree of swelling at the profile are summarized in Table 1.

[0049]

<Examples 5 to 8 (TMAH concentration: 0.1% by mass)>

The same operations as in Example 1 to 4 were conducted, except that the TMAH concentration of 0.05% by mass was changed to 0.1% by mass, to form a resist pattern. The resolution limit of the resulting resist pattern, cross sectional profile of the resist pattern, and resist pattern size, sensitivity and degree of swelling at the profile are summarized in Table 2.

[0050]

<Comparative Example 2 (TMAH concentration: 0.1% by mass)>

The same operation as in Comparative Example 1 was conducted, except that the

TMAH concentration of 0.05% by mass was changed to 0.1% by mass, to form a resist pattern. Resolution limit of the resulting resist pattern, cross sectional profile of the resist pattern, and resist pattern size, sensitivity and degree of swelling at the profile are summarized and shown in Table 2.

[0051]

<Examples 9 to 12 (TMAH concentration: 0.2% by mass)>

The same operations as in Examples 1 to 4 were conducted, except that the TMAH concentration of 0.05% by mass was changed to 0.2% by mass, to form a resist pattern. Resolution limit of the resulting resist pattern, cross sectional profile of the resist pattern, and resist pattern size, sensitivity and degree of swelling at the profile are summarized and shown in Table 3.

[0052]

<Comparative Example 3 (TMAH concentration: 0.2% by mass)>

The same operation as in Comparative Example 1 was conducted, except that the TMAH concentration of 0.05% by mass was changed to 0.2% by mass, to form a resist pattern. Resolution limit of the resulting resist pattern, cross sectional profile of the resist pattern, and resist pattern size, sensitivity and degree of swelling at the profile are summarized and shown in Table 3.

[0053]

<Examples 13 to 16 (TMAH concentration: 0.5% by mass)>

The same operations as in Examples 1 to 4 were conducted, except that the TMAH concentration of 0.05% by mass was changed to 0.5% by mass, to form a resist pattern. Resolution limit of the resulting resist pattern, cross sectional profile of the resist pattern, and resist pattern size, sensitivity and degree of swelling at the profile are summarized and shown in Table 4.

[0054]

<Comparative Example 4 (TMAH concentration: 0.5% by mass)>

The same operation as in Comparative Example 1 was conducted, except that the TMAH concentration of 0.05% by mass was changed to 0.5% by mass, to form a resist

pattern. The resolution limit of the resulting resist pattern, cross sectional profile of the resist pattern, and resist pattern size, sensitivity and degree of swelling at the profile are summarized and shown in Table 4.

[0055]

[Table 1]

(Concentration of developing solution: 0.05% by mass)

Examples or Comparative Examples	Polymer			Resolution limit (nm)	Resist pattern profile	Sensitivity (mJ/cm ²) evaluated by 1:1 L&S pattern of 180 nm	Swelling degree evaluated by 1:1 L&S pattern of 180 nm
	x:y or p:q	Mass-average molecular weight	Dispersion degree				
Example 1	69:31	2600	2.11	120	high orthogonality at 130 nm, good	21	none
Example 2	60:40	2900	1.65	120	high orthogonality at 130 nm, good	21	none
Example 3	51:49	2900	1.66	120	high orthogonality at 130 nm, good	19	none
Example 4	37:63	2900	2.04	120	high orthogonality at 130 nm, good	21	none
Comparative Example 1	68:32	2700	2.03	140	poor even at 180 nm	14.5	none

[0056]

[Table 2]

(Concentration of developing solution: 0.1% by mass)

Examples or Comparative Examples	Polymer x:y or p:q	Resolution limit (nm)	Resist pattern profile	Sensitivity (mJ/cm ²) evaluated by 1:1 L&S pattern of 180 nm	Swelling degree evaluated by 1:1 L&S pattern of 180 nm
Example 5	69:31 the same polymer as in Example 1	130	high orthogonality at 140 nm, good	21	none
Example 6	60:40 the same polymer as in Example 2	130	high orthogonality at 140 nm, good	20	none
Example 7	51:49 the same polymer as in Example 3	130	high orthogonality at 130 nm, good	19	none
Example 8	37:63 the same polymer as in Example 4	130	high orthogonality at 130 nm, good	21.5	none
Comparative Example 2	68:32 the same polymer as in Comparative Example 1	180	poor even at 180 nm	14.5	swelling observed

[0057]

[Table 3]

(Concentration of developing solution: 0.2% by mass)

Examples or Comparative Examples	Polymer x:y or p:q	Resolution limit (nm)	Resist pattern profile	Sensitivity (mJ/cm ²) evaluated by 1:1 L&S pattern of 180 nm	Swelling degree evaluated by 1:1 L&S pattern of 180 nm
Example 9	69:31 the same polymer as in Example 1	140	high orthogonality at 140 nm, good	21.5	none
Example 10	60:40 the same polymer as in Example 2	140	high orthogonality at 140 nm, good	20.5	none
Example 11	51:49 the same polymer as in Example 3	140	high orthogonality at 140 nm, good	19	none
Example 12	37:63 the same polymer as in Example 4	130	high orthogonality at 130 nm, good	23	none
Comparative Example 3	68:32 the same polymer as in Comparative Example 1	not resolved	impossible to form a pattern	impossible to evaluate	swelling observed

[0058]

[Table 4]

(Concentration of developing solution: 0.5% by mass)

Examples or Comparative Examples	Polymer x:y or p:q	Resolution limit (nm)	Resist pattern profile	Sensitivity (mJ/cm ²) evaluated by 1:1 L&S pattern of 180 nm	Swelling degree evaluated by 1:1 L&S pattern of 180 nm
Example 13	69:31 the same polymer as in Example 1	140	high orthogonality at 150 nm, good	21	slight swelling observed
Example 14	60:40 the same polymer as in Example 2	140	high orthogonality at 140 nm, good	20	none
Example 15	51:49 the same polymer as in Example 3	140	high orthogonality at 140 nm, good	19	none
Example 16	37:63 the same polymer as in Example 4	130	high orthogonality at 130 nm, good	24	none
Comparative Example 4	68:32 the same polymer as in Comparative Example 1	not resolved	impossible to form a pattern	impossible to evaluate	swelling observed

[0059]

As is apparent from the results shown in Table 1 to Table 4, in any case wherein the TMAH concentration of the developing solution is within a range from 0.05 to 0.5% by mass, the negative resist compositions of the Examples of the present invention exhibited a small resolution limit, a good resist pattern shape, high sensitivity and less swelling as compared with the Comparative Examples.

Thus, it could be confirmed that a good resist pattern can be obtained without causing swelling by using the negative resist compositions of the Examples of the invention.

[0060]

[Effects of the Invention]

As described above, the negative resist composition of the present invention is less likely to swell in an alkali developing solution and yields a good resist pattern.

[Document Type] Abstract

[Abstract]

[Problem to be Solved by the Invention]

Providing a negative resist composition less likely to swell in an alkali developing solution.

[Means of Solving the Problem]

An alkali-developable negative resist composition is disclosed comprising a compound (A) which generates an acid upon exposure to radiation, and a resin component (B) which becomes insoluble in alkali under the action of an acid, wherein the component (B) is a resin component containing: (b1) a unit which becomes insoluble in an alkali solution as a result of the formation of a lactone under the action of an acid generated from the component (A), and (b2) a unit having an alcoholic hydroxyl group.

[Selected Drawings] None